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SPECTROPHOTOMETRIC DETERMINATION OF CROTONALDEHYDE

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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ABSTRACT

A spectrophotometric method has been developed for the analysis of crotonaldehyde based on its reaction with 4-hexylresorcinol The product formed has two analytically useful absorption maxima at 385 and 345 mμ. The crotonaldehyde product obeys Beer's law in the 1 to 20 μg/ml range. Saturated aldehydes and ketones, alcohols, esters, acids, most hydrocarbons and phenols do not interfere significantly. Unsaturated aldehydes, unsaturated ketone and diolefins in excess interfere appreciably, as does nitrogen dioxide. Results of the analyses of a number of liquid mixtures are given.

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Crotonaldehyde has been identified in automobile exhaust gases,[7] cool flame combustion products,[5,7,9-11] and in tobacco smoke.[12,19] Analyses for crotonaldehyde also have been reported in vinyl acetate,[3,21] butyraldehyde,[8] alcohols,[13,14] butadiene condensates,[1] essential oils,[20] and various simple mixtures.[6,17]

These analyses have been accomplished by a variety of methods including ultraviolet analysis of the crotonaldehyde,[3,13,17] bromination[8] and iodometry,[18] bisulfite addition,[6] mercaptan addition,[2] infrared[15] and ultraviolet analysis of the 2,4-dinitrophenylhydrazone of crotonaldehyde[11,12,19] polarographic analysis,[5,10,11,21] gas chromatography,[7,9] and colorimetry.[1,14,20] Many of the methods used are not specific for crotonaldehyde or even for α,β-unsaturated aldehydes.

Crotonaldehyde can be separated and determined in the presence of other aldehydes by chromatographing the 2,4-dinitrophenylhydrazone derivatives and then applying ultraviolet analysis to the separated hydrazones.[12,19] Partial separation of the 2,4-dinitrophenylhydrazones by chromatographing the hydrazones followed by polarographic analysis of the zone containing crotonaldehyde, acrolein and propionaldehyde also permits the specific determination of crotonaldehyde.[11] Gas chromatography can be used to separate and analyze for crotonaldehyde in complex gas mixtures.[7,9] However, all of these methods are complex and time-consuming.

Benzidine hydrochloride[1] and m-phenylene diamine dihydrochloride[20] have been used as colorimetric reagents. However, they react not only with

crotonaldehyde but with other saturated and unsaturated aldehydes including formaldehyde.[16] Recently 4-hexylresorcinol has been used as the reagent in a spectrophotometric method for acrolein.[4,14] It was found that crotonaldehyde also reacts with 4-hexylresorcinol to form a product possessing a characteristic spectrum in the visible and ultraviolet regions.[4] Two of the bands in the ultraviolet can be used for quantitative analysis. Optimum reaction conditions have been evaluated. In the present work crotonaldehyde has been analyzed in many liquid mixtures containing large quantities of other aldehydes, ketones, alcohols, esters and phenols.

EXPERIMENTAL DETAILS

The materials used have been described elsewhere.[4] Readings of absorbance were made on both a Cary Model 11 Spectrophotometer and a Beckman Model B Spectrophotometer.

Solutions. -- The 4-hexylresorcinol solution contained 5 grams of 4-hexylresorcinol (m.p. 68-70°) dissolved in about 5 ml of 96% ethanol to give 10 ml of solution.

The mercuric chloride solution contained 3 grams of $HgCl_2$ in 100 ml of 96% ethanol.

Saturated trichloroacetic acid was prepared by dissolving 100 grams of the acid (reagent grade crystals) in 10 ml of water. The mixture was heated in a water bath until all of the trichloroacetic acid was dissolved. The resulting solution had a volume of about 70 ml.

Procedure for Liquid Samples . -- To 2.5 ml of ethanol containing the sample, 0.05 ml (about two drops) of the alcoholic 4-hexylresorcinol solution is added, then 0.2 ml of the 3% alcoholic mercuric chloride solution and 2.5 ml of the saturated aqueous trichloroacetic acid solution. A blank is similarly prepared. The resulting solution is heated for 20 minutes at 60°, removed from

the constant temperature bath and cooled to room temperature. The absorbance of the solution is read immediately at 385 mμ. Occasionally, it is advantageous to use the peak at 345 mμ. These absorption bands are relatively constant (± 1%) for 1½ hours of further reaction time.

Instead of heating, and equally acceptable procedure is to allow the solution to react at room temperature for one hour and then read the absorbance. The intensity of the 385 mμ peak is about 10% greater here than with heating, and the absorbance of the 385 mμ peak is relatively constant between 1 and 2 hours of reaction time.

RESULTS

Proportions of Reactants. -- The relative volumes of the reactant solutions were varied over nearly the same ranges as those used previously in determining optimum reaction conditions for acrolein.[4] The conditions for achieving maximum intensity for the crotonaldehyde product peak at 385 mμ are almost the same as the optimum conditions for acrolein. The only difference is a slight increase, about 5%, in intensity of the product peaks at both 385 and 345 mμ when 0.2 ml rather than 0.1 ml of 3% mercuric chloride solution is added. This change along with addition of 0.10 ml of 4-hexylresorcinol solution instead of 0.05 ml, increases the intensity of the 345 μ peak about 10%.

Nature of the Spectra of the Reaction Product. -- The product formed by the reaction of the crotonaldehyde with the 4-hexylresorcinol has a band system consisting of two weak bands with maxima at 540 and 495 mμ, and of two bands of moderate intensity with maxima at 385 and 345 mμ (Figure 1). These product absorption bands change only slightly in intensity over several hours. Over a 24-hour reaction period the band system changes appreciably (Figure 2).

The band farthest in the ultraviolet remains at about the same intensity, but its maximum shifts to 325 mμ. The peak of the other ultra-violet band remains at 385 mμ, but it decreases to about half of its maximum intensity. The band at 495 mμ continues to peak near the same wavelength. More significant is its four-fold increase in intensity. The band originally at 540 mμ becomes a shoulder on the other more intense band in the visible.

The absorbances of the maxima at 385 and 345 mμ are linear with concentration in at least the 10 to 200 μg range of crotonaldehyde in the reaction mixture. The absorptivities of the two maxima are very close. Both peaks of the crotonaldehyde product have absorptivities of 0.38 ± 0.02 μg^{-1} ml cm^{-1} based on the crotonaldehyde concentration in μg per ml of the reaction mixture.

Products Formed by Crotonaldehyde with Various Alkylresorcinols. -- The absorption spectra of the products formed by crotonaldehyde with 2-methylresorcinol, 4-ethylresorcinol, and 4-cyclohexylresorcinol were investigated. Crotonaldehyde reacts with 2-methylresorcinol to produce a very weak absorption spectrum characterized only by a very weak band at 405 mμ. 4-Ethylresorcinol reacts with crotonaldehyde to form a reaction product with an absorption spectrum having bands with maxima at about 535, 390 and 335 mμ. The intensity of these bands is about half the intensity of the bands associated with the product formed by crotonaldehyde with 4-cyclohexylresorcinol. The product formed by crotonaldehyde with 4-cyclohexylresorcinol has a band system with maxima at 540, 500, 385 and 340 mμ. These bands have intensities only slightly higher than those of the product formed by crotonaldehyde with 4-hexylresorcinol. Since no really significant advantage appeared to exist in using other 4-alkylresorcinols, 4-hexylresorcinol is the reagent of choice on the basis of availability and cost.

Reaction of Crotonaldehyde with 4-Hexylresorcinol in Trifluoroacetic Acid. -- Trifluoroacetic acid was substituted for trichloroacetic acid with all of the other reaction conditions held constant. The intensities of the peaks at 385 and 345 mμ decreased between 5 and 10%. Consequently, it appears that there is no advantage in the use of trifluoroacetic acid as a part of the reaction medium. A similar result was obtained with acrolein.[4]

Reaction Time and Temperature. -- The absorbances of reaction mixtures containing 100 μg of crotonaldehyde were measured over a several hour period after 0,5,10,15,20 and 30 minutes of heating at 60° C (Table I). Heating for periods of 20 or 30 minutes results in essentially maximum absorbance being attained at the end of the heating period. The absorbance remains constant for a total of one and a half hours of reaction and decreases very slowly during the next half hour. Reaction at room temperature necessitates a one hour reaction period to reach about the maximum absorbance. The absorbance is essentially constant (± 2%)during the next hour of reaction. Significant fading is beginning to occur under all reaction conditions after two hours of total reaction time.

Product Spectra in Ultraviolet of Other Aldehydes and Ketones. -- All of the other unsaturated aliphatic aldehydes form products with 4-hexylresorcinol having appreciable absorption in the 340 to 390 mμ region (Table II). The acrolein product has a weak maximum at 410 mμ. Fortunately, the residual absorption in the 340 to 390 mμ region, although appreciable, is small compared to the strong absorption in the 500 to 650 mμ region. α-Methylacrolein forms a product with a shoulder at about 410 mμ and a maximum around 325 mμ. The 385 mμ absorption maximum of the crotonaldehyde product occurs near an absorption minimum for the α-methylacrolein product, 2-methyl-2-butenal forms a weak product spectrum with a maximum at 390 mμ about one-fifth as intense as the maximum at 385 mμ possessed by the crotonaldehyde product.

In addition to the weak absorption maxima at 540 and 450 mμ in the products formed by saturated aliphatic aldehydes,[4] propanal and butanal have very weak maxima at 400 mμ. However, in the 340 to 390 mμ region the residual absorption is very small. Thousand-microgram quantities of saturated aldehydes have absorbances of less than 0.1 unit in the 340-390 mμ region. The absorptivities of a number of saturated aldehydes after about one hour reaction time are given in Table II. The amount of absorption is somewhat greater around 350 mμ owing to an absorption band common to the saturated aldehyde products far in the ultraviolet.

Furfural, cinnamaldehyde and benzaldehyde react to form products with moderately strong absorption, but having no absorption maxima in the 340 to 390 mμ region. Their products have about their minimum absorption between 360 and 390 mμ.

Glyoxal forms a product with no significant absorption below about 370 mμ. The methyl gloxal product has a weak maximum at 405 mμ, but the absorption is about at a minimum near 385 mμ. The products of both glyoxals have strong absorption bands below 350 mμ; consequently, the interference is greater with the 345 than the 385 mμ crotonaldehyde product maximum.

The products of saturated aliphatic ketones with 4-hexylresorcinol do not absorb in the visible and ultraviolet, $a < .0001\ \mu g^{-1}\ ml\ cm^{-1}$. The unsaturated ketone, 3-buten-2-one, forms a product having a weak absorption maximum at 395 mμ. This maximum is about one-tenth as intense as the 385 or 345 mμ maxima of the crotonaldehyde product. Since 3-buten-2-one appears to have no strong absorption farther in the ultraviolet, the 345 mμ maximum of the crotonaldehyde product is less interfered with than its 385 mμ maximum. The diketone, 2,3-butandione, reacts with 4-hexylresorcinol to form a product with weak absorption maxima at 550 and 415 mμ. The interference of 2,3-butandione with the 385 mμ maximum of the crotonaldehyde reaction product is small (Table II).

Product Spectra of Some Other Oxygenated Compounds in the Ultraviolet. A number of members of other classes of oxygenated compounds were reacted with the 4-hexylresorcinol reagent. The compounds used were acrylic acid, glyoxylic acid, n-butanol, glycerol, allyl alcohol, ethyl acetate, propyl acetate, vinyl acetate, phenol, o-cresol and m-cresol. Most of these compounds showed no appreciable absorption in the 340 to 390 mμ region. Their absorptivities usually were 0.0001 μg^{-1} ml cm^{-1} or less. Glyoxylic acid did react to form a weak maximum at 540 mμ, and both glyoxylic and acrylic acid products absorbed somewhat below 350 mμ (Table II). In general, it appears possible to analyze for crotonaldehyde in the presence of large excesses of these classes of oxygenated compounds.

Product Spectra of Some Hydrocarbons in the Ultraviolet. -- 1,3-Butadiene, 2-methyl-1,3-butadiene and 1,3-butadiene react with the reagent to form products with weak absorption maxima at 400 to 405 mμ. Their absorption is at a minimum near 375-380 mμ and then increases appreciably below 350 mμ. The interference of diolefins is somewhat less for the 385 mμ maximum than for the 345 mμ maximum of the crotonaldehyde product (Table II).

m-Xylene and other alkylbenzenes do not react significantly with 4-hexylresorcinol. The absorptivity for the m-xylene product is less than 0.0001 μg^{-1} ml cm^{-1} between 300 and 700 mμ.

Product Spectra of Nitrogen Dioxide in the Ultraviolet. It has been pointed out elsewhere that nitrogen dioxide reacts with 4-hexylresorcinol to form a yellow product with a strong absorption maximum at 310-320 mμ. This maximum overlaps both the 345 and the 385 mμ maximum of the product crotonaldehyde forms with 4-hexylresorcinol. Consequently, one should expect serious interference by nitrogen dioxide in the analysis of crotonaldehyde by the present method.

Analysis of Liquid Mixtures. -- A considerable number of liquid mixtures containing crotonaldehyde in combination with excess amounts of other components were analyzed for crotonaldehyde content. The compositions of the mixtures as prepared, along with the crotonaldehyde content as analyzed, are given in Table III. In most of the mixtures large enough amounts of the other components were used so as to present a small interference to the analysis of crotonaldehyde by the present method.

Mixture A contains about a ten-fold excess of mixed saturated aldehydes while mixture B contains a five-fold excess of propanal. In both analyses the crotonaldehyde found is about 3% higher than the amount actually present because of the small background absorption of the saturated aldehydes. Consequently, the ratios of crotonaldehyde to lower saturated aldehydes should be 1 to 10 or less, and to higher saturated aldehydes should be 1 to 5 or less, if an accurate quantitative analysis is necessary.

Crotonaldehyde can be determined in large excesses of alcohols, ketones, esters and phenols. This is shown by the analyses of mixtures C,D and E. One should be able to analyze for crotonaldehyde in mixtures containing up to at least 100-fold total excesses of various components from the classes of oxygenates listed in mixture C.

A more difficult analytical problem is encountered when crotonaldehyde is sought in mixtures containing other unsaturated components such as acrolein, 1,3-pentadiene, benzaldehyde and furfural. In each of these analyses, although the other component is present at much lower concentrations than the saturated oxygenated materials in the previous analyses, significant background absorption occurs. The background absorption sometimes can be corrected by using the concentration of the other component obtained from its product absorption band, i.e., acrolein, 605 mμ; 1,3-pentadiene, 605 mμ;

furfural, 640 mμ. Except for acrolein, the correction would be only approximate since the 605 mμ band of the 1,3-pentadiene product and the 640 mμ band of the furfural product do not obey Beer's Law at all satisfactorily. The crotonaldehyde-furfural analysis is one of the few analytical situations for which the 345 mμ band of crotonaldehyde is more satisfactory than the 385 mμ band. In these analyses as well as others involving components such as α-methylacrolein or 3-buten-2-one the present method of quantitative analysis will be satisfactory only if the other unsaturated components are present in about the same concentration as the crotonaldehyde.

DISCUSSION

4-Hexylresorcinol appears to be the first colorimetric reagent with even fair specificity towards crotonaldehyde. Other unsaturated aldehydes if present in about equal amounts will interfere appreciably. However, the method has good selectivity when the crotonaldehyde is to be determined in the presence of saturated aldehydes or ketones, saturated or unsaturated alcohols, esters, acids or phenols. The absorption peaks are only about one-tenth the intensity of the acrolein product band at 605 mμ. Consequently, the method for crotonaldehyde is much less sensitive than the method described elsewhere for acrolein.

The serious interference of nitrogen dioxide with the determination of crotonaldehyde is unfortunate. This interference prevents the use of the method for analyzing crotonaldehyde in combustion sources producing appreciable quantities of nitrogen oxides. This is in contrast to the successful application of the general method to acrolein in combustion sources.[4] The difference in applicability is the result of the presence of the crotonaldehyde product bands in the ultraviolet rather than in the visible, and of their lower intensities.

LIST OF FIGURES

Figure I. Absorption spectrum of product formed after one hour of reaction between 54 µg of crotonaldehyde and 4-hexylresorcinol reagent.

Figure II. Absorption spectrum of product formed after 22 hours of reaction between 54 µg of crotonaldehyde and 4-hexylresorcinol reagent.

REFERENCES

1. Alekseev, S.V., Sintet Kauchuk 10, 13-16 (1936).
2. Beesing, D.W., Tyler, W.P., Kurtz, D.M., Harrison, S.A., Anal. Chem. 21, 1073 (1949).
3. Capitani, C., Milani, E., Chimica e industria 37, 177 (1955).
4. Cohen, I.R., Altshuller, A.P., Anal. Chem., to be published.
5. Dobrinskaya, A.A., Nieman, M.B., Rudnevskii, N.K., Zhur. Fiz. Khim. 27, 1572 (1953).
6. Hähnel, S., Lennerstrand, M., Svensk Kem Tids 53, 336 (1941).
7. Hughes, K.J., Hurn, R.W., "A Preliminary Survey of Hydrocarbon-Derived Oxygenated Material in Automobile Exhaust Gases," Presented at the 53rd Annual Meeting of the Air Pollution Control Association, Cincinnati, Ohio, May 22-26, 1960.
8. Kubias, J., Pilny, S., Chem. Listy 47, 672 (1953).
9. Kyryacos, G., Menapace, H.R., Boord, C.E., Anal. Chem. 31, 222 (1959).
10. MacNevin, W.M., Urone, P.F., Omietanski, M.L.B., Dunton, M.L., "Polarographic Study of Cool-Flames Oxidation Products of Hydrocarbons" in Fifth Symposium (International) on Combustion. Reinhold Publishing Corp., New York, N.Y., 1955, pp. 402-5.
11. Malmberg, E.W., Smith, M.L., Bigler, J.E., Bobbitt, J.A., "A Study of Cool Flames and Associated Reactions in an Engine," Ibid. pp. 389-91.
12. Mold, J.D., MacRae, M.T., Tobacco 144, 24 (1957).
13. Nishi, N., Hakkô Kyôkaishi 15, 429 (1957).
14. Rosenthaler, L., Vegezzi, G., Z. Lebensm. -Untersuch. u.-Forsch 99, 352 (1954).
15. Ross, J.H., Anal. Chem. 25, 1288 (1953).
16. Snell, F.D., Snell, C.T., Colorimetric Methods of Analysis, Vol. II., D. Van Nostrand Co., Inc. New York, N.Y., 1937, pp. 61-70

References cont.

17. Stolyarov, K.P., Ivanor, V.S., Zhur. Anal. Khim., 13, 246 (1958).

18. Veksler, R.I., Trudy Komissii Anal. Khim. Acad. Nauk S.S.S.R. 3, 369 (1951).

19. Wahl, R., Tabak-Forsch Wiss. Beil. Süddeut. Tabakztg. 22, 61 (1957).

20. Wearn, R.B., Murray, W.M., Jr., Ramsey, M.P., Chandler, N., Anal. Chem. 20, 922 (1948).

21. Yano, M., Matsunoto, M., J. Chem. Soc. Japan (Ind. Chem. Section) 55, 498 (1952).

TABLE I. EFFECT OF HEATING AND REACTION TIME ON INTENSITY OF ABSORPTION AT 385 mμ

Heating period, minutes[b]	End of heating period	Absorbance after total reaction time of - 30 min.	45 min.	60 min.	90 min.	120 min.
0	--	0.55	0.72	0.79	0.81	0.73
5	0.33	.62	.73	.78	.79	.75
10	.62	.68	.74	.74	.74	.72
15	.70	.72	.74	.75	.75	.71
20	.73	.74	.74	.74	.74	.71
30	.74	.74	.74	.74	.72	.71

a Absorbance for 100 μg of crotonaldehyde in reaction mixture.

b Heated at 60° for the time indicated

TABLE II. ABSORPTIVITIES FOR PRODUCTS OF VARIOUS OXYGENATES AND HYDROCARBONS WITH 4-HEXYLRESORCINOL REAGENT

Substance	a. Absorptivities,[a] μg^{-1} ml cm^{-1}	
	385 mμ	345 mμ
crotonaldehyde	0.038	0.038
acrolein	.01	.01
α-methylacrolein	.007	.014
2-methyl-2-butanal	.007	.007
formaldehyde	.0001	.0003
acetaldehyde	.0001	.0003
propanal	.0002	.0002
butanal	.0003	.0002
2-methylpropanal	.0004	.0008
furfural	.003	.003
cinnamaldehyde	.005	.008
benzaldehyde	.001	.002
glyoxal	<.0001	.002
methylglyoxal	.0004	.002
aliphatic ketones	<.0001	<.0001
3-buten-2-one	.004	.001
2,3-butandione	.0005	.001
acrylic acid	.0003	.0006
glyoxylic acid	.0002	.0004
butanol	<.0001	<.0001
glycerol	.0001	.0002
allyl alcohol	.0001	.0002

Table II. cont.

Substance	Absorptivities,[a] μg^{-1} ml cm^{-1} 385 mμ	345 mμ
phenols	<0.0001	<0.0001
aliphatic esters	<0.0001	<0.0001
1,3-butadiene	.0005	.001
2-methyl-1,3-butadiene	.0003	.0006
1,3-pentadiene	.001	.002
alkylbenzenes	<0.0001	<0.0001

a Absorptivities for 100 to 1000 μg quantities of substances listed, after heating for 20 minutes at 60° and about one hour total reaction time with reagents.

TABLE III. ANALYSES OF VARIOUS LIQUID MIXTURES FOR CROTONALDEHYDE

Mixture	Composition, as prepared: Substance	Concn., µg	Concn., µg of Crotonaldehyde as analyzed at 385 mµ [a]
A	crotonaldehyde	54.5	56
	formaldehyde	211	
	acetaldehyde	115	
	propanal	62	
	butanal	63	
	2-methylpropanal	42	
B	crotonaldehyde	48.5	50
	propanal	260	
C	crotonaldehyde	54.5	55.5
	aliphatic alcohols	2140	
	aliphatic ketones	2170	
	aliphatic esters	1970	
	phenols	2610	
D	crotonaldehyde	54.5	56.5
	n-butanol	98	
E	crotonaldehyde	48.5	48.5
	vinyl acetate	926	
F	crotonaldehyde	58	66
	acrolein	18	
G	crotonaldehyde	48.5	53
	1,3-pentadiene	99	

Table III cont.

Mixture	Composition, as prepared Substance	Concn., μg	Concn., μg of crotonaldehyde as analyzed at 385 mμ [a]
H	crotonaldehyde	48.5	51.5
	benzaldehyde	223	
I	crotonaldehyde	48.5	55.5 [b]
	furfural	54.5	

a No correction made for background absorption of other components.

b Use of 345 mμ maximum gives a crotonaldehyde concn. of 51.5 μg.